Mode Mixing of Liquid Surface Waves

J. C. Earnshaw and E. McCoo
The Department of Pure and Applied Physics, The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland

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High frequency capillary waves on the surface of dilute aqueous solutions of cetyltrimethylammonium bromide have been studied by quasielastic light scattering. The wave propagation deviates significantly from classical expectation, due to enhanced coupling between the capillary and dilational modes of the surface. At a concentration of 0.04mM the capillary wave behavior clearly demonstrates mixing of these two surface modes. The effects appear to derive from a reduction in the stability of the dilational waves.

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The modes of fluid interfaces and their stability have long been subjects of scientific investigation. The modes of present concern are the capillary ripples governed by surface tension, and the dilational modes sustained by the elastic properties of a surface covered by a molecular film [1]. In linear treatments of stability these modes have commonly been regarded as independent [2,3], but they are in fact coupled. While some effects of the coupling are well established [4], unexpected consequences, such as mode mixing, have recently been predicted [5,6]. In certain circumstances the two branches of the surface wave dispersion equation [4] split, one evolving from capillary to dilational in nature, and vice versa. Between these extremes mixed modes, neither capillary nor dilational, are predicted.

This Letter presents experimental data demonstrating, for the first time, manifest mode mixing between capillary and dilational waves at liquid surfaces. The observation of such consequences of the mode coupling emphasizes that it cannot be neglected, as has often been done in considerations of surface mode stability [2,3]. The data support recent predictions of destabilization of the dilational modes [3]: Both the capillary wave dispersion and negative effective values of the dilational surface viscosity, inferred independently by direct data analysis, can be understood only if there exists a destabilizing influence acting upon the dilational modes.

Quasielastic light scattering has been used to study the dispersion behavior of thermally excited capillary waves [7]. The wave amplitudes are so low that linear theory suffices. The correlation function of the scattered light at a particular wave number q, the Fourier transform (FT) of the spectrum of the capillary waves [8], can be analyzed to yield an unbiased estimate of the complex frequency of the waves ($\omega = \omega_0 + i\Gamma$) [9]. For pure fluids the measured dispersion behavior accords excellently with expectation based on the known fluid properties, but this agreement is less evident in studies of solutions of various ionic surfactants [10].

Here we concentrate on aqueous solutions of the cationic surfactant cetyltrimethylammonium bromide (C_{16}TAB) at 25 °C, for which we have systematically studied a wide range of concentrations. For all concentrations below the critical micelle concentration (cmc $= 0.92$mM) the light scattering data (ω_0, Γ) departed from the accepted capillary wave dispersion behavior at high q. The effects were entirely reproducible. They were greatest at about 0.04mM CTAB, and we therefore concentrate upon that region.

Figure 1 shows capillary wave data for three different concentrations. The lines represent the behavior predicted for a fluid of tension 70 mN/m (appropriate to these dilute solutions), other properties, both surface and bulk, being as for water. In general, the measured ω_0 was close to expectation over much of the q range, whereas the capillary Γ at low and modest q was higher than expected for a free liquid surface because of the coupling

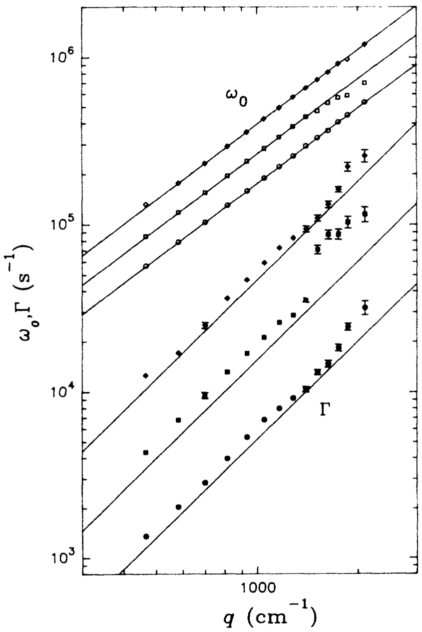

FIG. 1. Capillary wave frequencies (open symbols) and damping values (full symbols) for three different CTAB solutions: ○, 0.035mM (ω_0 scaled down by 1.5 and Γ by 3); □, 0.04mM; ◇, 0.045 mN (ω_0 scaled up by 1.5 and Γ by 3). The lines are theoretical predictions for a fluid of tension 70 mN/m, other properties being as for water at 25 °C.

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to the dilational waves [4]. However, Γ departed significantly from the expected trend ($\propto q^2$) above 1200 cm^{-1}. The most marked effects are those for 0.04mM, for which a discontinuous jump in Γ coincided with a significant decrease in ω_0 at $q \approx 1500\ \mathrm{cm}^{-1}$. For the other concentrations shown Γ fell off from the trend extrapolated from $q < 1200\ \mathrm{cm}^{-1}$, followed by a recovery towards that trend at the highest q studied. Similar effects to those shown for 0.035mM and 0.045mM were found for all concentrations below the cmc. In all cases the perturbations of Γ set in for frequencies $\omega_0 \approx 3\times10^5\ \mathrm{s}^{-1}$. Such marked changes in dispersion behavior have never been reported for any other systems, although a decrease in Γ such as that at 1200 cm^{-1} for 0.035mM CTAB has been noted in very dilute solutions of n-heptanol [6]. The present effects must reflect physical processes in the CTAB solutions which affect the capillary waves.

The capillary and dilational waves constitute coupled oscillators [4–6] and the effects appear to arise from this coupling. The coupling is most apparent in Kramer's analysis of a film-covered liquid surface [11]. The dispersion equation of the surface waves relates their temporal evolution ($\omega = \omega_0 + i\Gamma$) to the surface wave number q. The two physical roots correspond to capillary waves governed by surface tension γ and to dilational modes governed by the dilational modulus ε ($= -d\gamma/d\ln\Gamma_s$, Γ_s being the surface excess surfactant concentration) of the surface film [11]. Because of the coupling the capillary wave propagation is affected by both of these moduli. Dissipative effects within the surface film can be incorporated by expanding the surface moduli as linear response functions [12]: $\gamma = \gamma_0 + i\omega\gamma'$ and $\varepsilon = \varepsilon_0 + i\omega\varepsilon'$. The principal effect of the surface viscosities γ' and ε' is to increase the dissipation (and hence Γ) of the capillary and dilational modes, respectively [5].

The best established result of the coupling is the resonance between the two modes [4], which occurs at $\varepsilon_0 \approx 0.16\gamma_0$ for experimentally accessible q. For coupled oscillators which are damped, as here, manifest mode mixing (as in simple coupled vibrators) arises when the damping constants of the two modes come together, whereupon the real frequencies separate [13].

In the present situation the damping of the dilational waves generally exceeds that of the capillary waves. Nonzero γ' increases the capillary Γ; the convergence of the two Γ values leads to stronger coupling and hence, for γ' above a critical value, to mixing [5]. The dilational surface viscosity ε' increases the dilational Γ, causing the complex frequencies of the two modes to diverge, rendering mode mixing less, rather than more, probable. However, $\varepsilon' < 0$ would cause the two Γ values to converge as the dilational Γ falls; the coupling again increases, and manifest mode mixing may be induced if $|\varepsilon'|$ exceeds a critical value [6]. We consider the significance of negative ε' below.

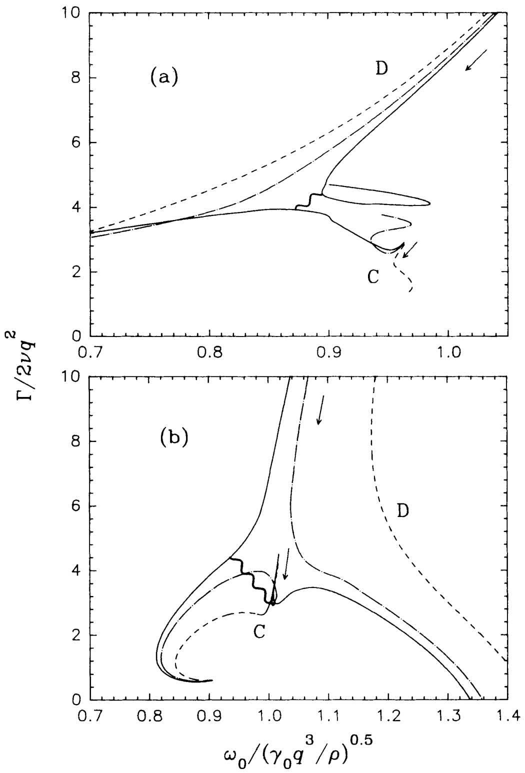

FIG. 2. Theoretical surface wave dispersion ($100 < q < 4000\ \mathrm{cm}^{-1}$, q increasing in direction of arrows) for two cases, showing the progression to mode mixing. Dilational waves denoted D, capillary waves C. Frequencies and damping values for both modes are normalized by the approximate *capillary* wave values. (a) $\gamma_0 = 65$ mN/m, $\varepsilon_0 = 15$ mN/m, $\varepsilon' = 0$, and $\gamma' = 0$ (dashed lines), 2×10^{-5} (chain lines), and 3×10^{-5} mN s/m (solid lines). (b) $\gamma_0 = 70$ mN/m, $\gamma' = 0$ mN s/m, $\varepsilon' = -2\times10^{-5}$ mN s/m, and $\varepsilon_0 = 15$ (dashes), 13 (chain), and 12.5 mN/m (solid). In both cases the chain lines indicate less coupled behavior; the solid lines show mode mixing. The wavy lines are discussed in the text.

Figure 2 illustrates these two routes to mode mixing, showing the complex frequencies of both modes from the dispersion equation [4,11], normalized by the first order approximations for the *capillary* waves: $\omega_0 \approx (\gamma_0 q^3/\rho)^{1/2}$ and $\Gamma \approx 2\nu q^2$ [11], where ν is the kinematic viscosity. The capillary mode should thus have normalized frequencies ~ 1, the coupling causing the damping to exceed unity. In both parts of Fig. 2 the progression from dashed, through chain, to solid lines indicates an increase in the coupling, resulting in mode mixing (solid lines). The physical parameters used in these computations were chosen to illustrate the effects, rather than for their applicability to the present data.

It is worth briefly reviewing the processes at work in Fig. 2. The dashed lines are furthest from mode mixing. In Fig. 2(a), for $\gamma' = 0$ (dashed lines) the normalized capillary ω_0 remains close to 1, the normalized Γ falling as q increases, while the dilational mode sweeps diagonally across the entire plot. Increasing γ' raises the capillary

Γ, that for the dilational mode being attracted down by the coupling (chain lines). Finally, for γ' above a critical value, initially capillary-type behavior evolves with increasing q into dilational type, and vice versa (solid lines): the observable capillary waves must make a transition from one branch to the other at some intermediate q. The situation in Fig. 2(b) is somewhat different; the increasing coupling leads to mode mixing arising as ε_0 approaches the resonant condition ($\approx 0.16\gamma_0$), negative ε' being held constant.

Such a plot of the surface wave dispersion points up the differences between the two routes to mode mixing. For mixing induced by γ', the observable capillary ω (normalized) should move left in the complex plane with increasing q, a discontinuous jump up at some q leading to a trend to the right. For mixing induced by $\varepsilon' < 0$, the normalized capillary ω moves vertically down before increasing discontinuously, thereafter tending down and to the left. These jumps of the capillary wave dispersion are schematically indicated in Fig. 2 by wavy lines. Plotting experimental data in this way should thus enable identification of the route to mode mixing.

Figure 3 shows such a plot of the normalized 0.04mM data of Fig. 1. While the absolute values of Γ are lower than those of Fig. 2(b) (see below for discussion), the data qualitatively accord essentially exactly with the description given above for mixing due to $\varepsilon' < 0$: ω moves down in the complex plane before Γ increases by about $\times 2$, ω then moves down and to the left. The variations of the normalized 0.035mM and 0.045mM data in the complex plane (not shown) resemble the chain line of Fig. 2(b) for the capillary mode, indicating that the system properties are close to but are not quite those for mode mixing. The 0.04mM data constitute the first observation of manifest mode mixing in waves on fluid surfaces.

We now turn to the interpretation of negative values of the dilational surface viscosity. If the surface viscosities were surface excess quantities [12], they might physically be negative. However, we regard $\varepsilon' < 0$ as an effective parameter, implying a reduction in the dilational Γ. Such a reduction in damping suggests that the stability of this mode is affected by some process or processes in the system. It has recently been shown [2,3] that for soluble surfactants, competition of various processes, such as convection or surface adsorption-desorption kinetics, with diffusional interchange between surface and bulk may, under certain circumstances, reduce the stability of the dilational waves. The effects occur at different characteristic frequencies, depending on the processes [3]: For example, competition with adsorption effects can significantly reduce the stability of dilational waves at frequencies $\sim 10^5$ s^{-1}, diminishing Γ for these modes [3]. We note that this value is close to that at which changes in the capillary Γ are experimentally evident (see Fig. 1).

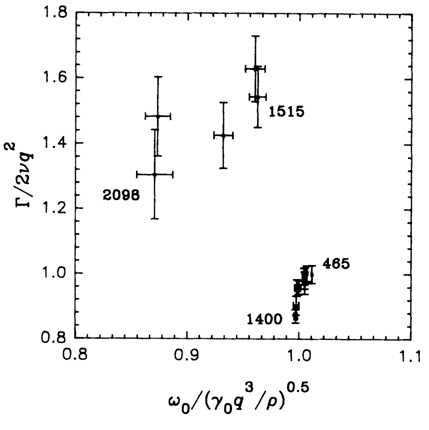

FIG. 3. The 0.04mM data of Fig. 1 normalized and plotted in the complex plane. The numbers indicate selected q values. The surface wave number varies from 465 to 2098 cm^{-1} as indicated by the numbered points.

Extension of the surface wave dispersion equation to accommodate the competing processes necessitates enlargement of the set of physical properties [3]. Many of these properties are not well established [3] and the modified dispersion equation cannot be solved for comparison with the present experimental data. However, "effective" values of the surface moduli γ and ε (i.e., the four parameters γ_0, γ', ε_0, and ε') can be estimated [14] by fitting the observed correlation functions directly with the FT of the established spectrum of thermally excited capillary waves on a film covered surface [8], based on the conventional dispersion equation [11]. For all of the present data for CTAB, such fits yielded unique negative values of ε', greater than their uncertainties. The data analysis excluded positive values of ε'. This does not accord with experience for *insoluble* surfactants [15], for which ε' is always ≥ 0 within errors, although negative values of the effective ε' have been found for other soluble surfactants [16]. The role of $\varepsilon' < 0$ as an effective parameter simulating the destabilizing of the dilational mode has been discussed elsewhere [6].

In summary, perturbations of the capillary wave propagation observed for $q > 1200$ cm^{-1} are consistent with the behavior expected for coupled surface modes, provided that the dilational wave stability is somewhat impaired. Analysis of the light scattering data at *all* q yields effective dilational surface viscosities which are negative. Such negative ε' implies that certain processes in the system reduce the dissipation, and hence Γ, of the dilational modes. The two independent analyses thus point to the same conclusions.

The Γ values of Fig. 3 are lower than those of Fig. 2(b) because the surface waves on the 0.04mM CTAB solutions are further from resonance than was assumed in the computations for Fig. 2(b). It is somewhat surprising that the effects of mode coupling are so strong for the present very low concentrations: the resonance between the surface modes occurs at 0.08mM, indicating maximal coupling there. These discrepancies likely derive from the approximate nature of the simulation of the dilational wave destabilization by $\varepsilon' < 0$, noted by [6]. Indeed, the dispersion equation for surface waves [4] would not yield mode mixing for the surface properties of the present data (inferred as described above). However, these surface properties, particularly $\varepsilon' < 0$, are effective values, derived by force fitting the observed photon correlation functions with a form [8] which does not properly incorporate all processes involved in surfactant solutions [3]. If all parameters of the full theory were known, ε' would presumably be positive and the reduction in dilational wave damping would rise from other processes. Mode mixing might then occur at lower ε_0 than in Fig. 2(b). The general agreement of the forms of the data of Fig. 3 and the solid lines of 2(b) supports the suggestion [6] that the gross features of such a full calculation would accord with the present predictions for $\varepsilon' < 0$. These differ so markedly from those of Fig. 2(a), representing the only other known route to mode mixing, that our identification of the actual route involved seems secure.

The observed consequences of the coupling at lower concentrations are very concentration dependent: compare the behavior for 0.035mM and 0.045mM with the manifest mode mixing apparent for 0.04mM. However, viewed as a consequence of mode coupling, the 0.04mM data differ only in degree from those at neighboring concentrations which also show the effects of the coupling rather strongly. It is possible that the sharpness of the concentration dependence of the effects is due to a phase transition in these very dilute adsorbed surface films [17], which could well give rise to very concentration dependent surface properties.

The demonstration that significant consequences of surface wave coupling may arise even in the linear regime emphasizes that it cannot be correct to ignore this coupling. This will require some reconsideration of theories of surface wave stability, in which the coupling is often neglected (e.g., [2,3]).

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